1.0 Title

**Standard Operating Procedure for the Determination of Metals and Trace Metals in Water and Wastes by Inductively Coupled Plasma-Atomic Emission Spectroscopy**

2.0 Scope and Application

2.1 The role of the inductively coupled plasma in analytical atomic spectroscopy is that of a stable, high temperature excitation source for atomic emission. Elements which are easily atomized tend to exhibit superior or equivalent detection limits compared to flame atomic absorption. Elements which are more difficult to atomize tend to give better detection limits in the higher temperature environment of the ICP. Interferences, analyte wavelength, wavelength range characteristics and sample preparation or matrix should be considered before an analysis is done.

2.2 This method is presently applicable to the following analytes:

| | | |
|---|---|---|
| Aluminum | Copper | Selenium |
| Antimony | Iron | Silica |
| Arsenic | Lead | Silver |
| Barium | Lithium | Sodium |
| Beryllium | Magnesium | Strontium |
| Boron | Manganese | Thallium |
| Cadmium | Molybdenum | Tin |
| Calcium | Nickel | Titanium |
| Chromium | Phosphorus | Vanadium |
| Cobalt | Potassium | Zinc |

2.3 This method provides procedures for determination of dissolved elements in ground waters, surface waters, and drinking water supplies. It may also be used for determination of total recoverable element concentrations in these waters and waste waters and, with the exception of silica, in sediments, solid waste samples, paints, tclp samples, and fish. This method is applicable to the analysis of drinking water for the primary analytes barium, beryllium, copper, and nickel; and the secondary analytes aluminum, calcium, iron, magnesium, manganese, potassium, silver, sodium, and zinc without preconcentration.

2.4 The wavelengths listed in Table 3 are recommended for these analytes. Also listed in Table 3 are typical instrument detection limits (IDLs) determined using reagent acid, ASTM type I water and conventional pneumatic nebulization sample

introduction into the plasma. These IDLs are intended as a guide and may vary depending on selected operating conditions. Table 2 also includes information on the linear range of the analytes and the precision of the analysis. Wavelengths and background correction methods other than those recommended may be substituted if they provide the needed sensitivity and are properly corrected for interelement spectral interferences.

2.5 Method limitations

2.5.1 Dissolved elements are determined after suitable filtration and acid preservation. Acid digestion procedures (See SOP I-1-32) are required prior to the determination of total recoverable elements. To reduce the potential of interferences, dissolved solids should be < 0.2% (w/v) [approximately 2000 mg/L].

2.5.2 When using this method for determination of boron and silica in aqueous samples, only plastic, Teflon or quartz labware should be used from time of sample preparation to completion of analysis. For accurate determinations of boron in solid sample extracts at concentrations below 100 mg/kg, only quartz beakers should be used in the digestion with immediate transfer of an extract aliquot to a plastic centrifuge tube following dilution of the digestate to volume. For these determinations, borosilicate glass must not be used in order to avoid sample contamination of these analytes from the glass.

2.5.3 This method is suitable for determination of silver in aqueous samples containing concentrations up to 0.1 mg/L. For the analysis of wastewater samples containing higher concentrations of silver, succeeding smaller volume, well mixed aliquots should be prepared until the analysis solution contains < 0.1 mg/L silver.

2.5.4 The sample preparation procedures given in SOPs I-1-31 and I-1-32 will solubilize and hold in solution only minimal concentrations of barium, as barium sulfate. In addition, the stability of soluble barium is greatly affected when free sulfate is available in solution. For more accurate determinations of barium in samples having varying and unknown concentrations of sulfate, samples should be analyzed as soon as possible after sample preparation is completed.

2.5.5 With the exception of silver, where this method is approved for the determination of certain metal and metalloid contaminants in drinking water, samples may be analyzed directly by pneumatic nebulization without acid digestion if the sample has been properly preserved with acid and has

turbidity of <1 NTU at the time of analysis.

2.5.6 This method is restricted to use by or under the supervision of analysts experienced in operating an ICP.

3.0 Summary of method: This method describes a technique for simultaneous multielement determination of metals and trace elements in solution. The basis of the method is the measurement of atomic emission by an optical spectrometric technique. Samples are nebulized and the aerosol that is produced is transported to the plasma torch where desolvation and excitation occur. Characteristic atomic-line emission spectra are produced by a radio-frequency inductively coupled plasma (ICP). The Optima 3000 optical design combines an echelle polychromator with a solid-state detector in an integrated system optimized for ICP_OES. The optical system is divided into two channels, one for the ultraviolet range and one for the visible range. There are two solid-state detectors, one used for each range. The polychromator has an echelle grating ruled at 79 lines/mm and a blaze angle of 63.4 degrees. It is designed to use multiple diffraction orders. To separate the orders and create a two-dimensional diffraction pattern, the echelle grating is combined with a cross-dispersing element. A Schmidt Cross Disperser is used in the ultraviolet range and a prism is used in the visible range. The Segmented-array, Charge-coupled-device Detector (SCD), is a solid-state imaging device. It provides simultaneous detection of over 5000 emission lines with simultaneous background measurement. A background correction technique is required to compensate for the variable background contribution to the determination of the analytes. Background must be measured adjacent to analyte lines on samples during analysis. The position used must either be free of spectral interference or adequately corrected to reflect the same change in background intensity as occurs at the analyte wavelength measured. Background correction is handled automatically by the instrument. The possibility of additional interferences mentioned below should also be recognized and appropriate corrections made.

4.0 Definitions: The definitions and purposes below are specific to this method, but have been conformed to common usage as much as possible.

4.1 Dissolved Analyte: The concentration of analyte that will pass through a 0.45 um membrane filter assembly prior to sample acidification.

4.2 Total Recoverable: The concentration of an analyte determined in an unfiltered sample following treatment by refluxing with hot, dilute mineral acid. (SOP I-1-32).

4.3 Instrumental Detection Limit (IDL): The concentration equivalent to the analyte signal which is equal to three times the standard deviation of a series of ten replicate measurements of a reagent blank signal at the same wavelength.

4.4 Method Detection Limit (MDL): The minimum concentration of an analyte that can be identified, measured and reported with 99% confidence that the analyte concentration is greater than zero.

4.5 Linear Dynamic Range (LDR): The concentration range over which the analytical curve remains linear.

4.6 Method of Standard Addition: The standard addition technique involves the use of the unknown and the unknown plus a known amount of standard.

4.7 Laboratory Reagent Blank (LRB): An aliquot of reagent water that is treated exactly as a sample including exposure to all glassware, equipment, reagents, and acids that are used with other samples. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents or apparatus.

4.8 Calibration Blank: A volume of ASTM type I water acidified with the same acid matrix as in the calibration standards. The calibration blank is used to calibrate the ICP instrument.

4.9 Stock Standard Solution: A concentrated solution containing one analyte purchased from a reputable commercial source. Stock standard solutions are used to prepare calibration solutions and other needed analyte solutions.

4.10 Calibration Standard (CAL): A solution prepared from the dilution of stock standard solutions. The CAL solutions are used to calibrate the instrument response with respect to the analyte concentration.

4.11 Instrument Performance Check Solution (IPC): A solution of method analytes, used to evaluate the performance of the instrument system.

4.12 Spectral Interference Check Solution (SIC): A solution of selected method analytes of higher level concentrations which is used to evaluate the procedural routine for correcting known interelement spectral interferences with respect to a defined set of method criteria.

4.13 Laboratory Fortified Blank (LFB): An aliquot of reagent water to which known quantities of the method analytes are added in the laboratory. The LFB is analyzed exactly like a sample, and its purpose is to determine whether method performance is within acceptable control limits.

4.14 Laboratory Fortified Sample Matrix (LFM): An aliquot of an environmental sample

to which known quantities of the method analytes are added in the laboratory. The LFM is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFM evaluated based on the concentrations found.

4.15 Quality Control Sample (QCS): A solution of method analytes of known concentrations which is used to fortify an aliquot of LRB matrix. The QCS is obtained from a source external to the laboratory, and is used to check laboratory performance.

4.16 Internal Standard: Pure analyte(s) added to sample, extract, or standard solution in known amount(s) and used to measure the relative responses of other method analytes that are components of the same sample or solution. The internal standard must be an analyte that is not a sample component.

4.17 Water sample: For the purpose of this method, a sample taken form one of the following sources: surface, ground, storm runoff, industrial or domestic wastewater.

4.18 Units of weights and measures: g gram, mg milligram, ug microgram, l liter, ml milliliter, ul microliter, um micrometer (10-6).

4.19 May: This action, activity, or procedural step is neither required nor prohibited.

4.20 May not: This action, activity, or procedural step is prohibited.

4.21 Must: This action, activity, or procedural step is required.

4.22 Shall: This action, activity, or procedural step is required.

4.23 Should: This action, activity, or procedural step is suggested, but not required.

5.0 Interferences

5.1 Spectral interferences: Can be categorized as an overlap of a spectral line from another element; unresolved overlap of molecular band spectra; background contribution from continuous or recombination phenomena; or background contribution from stray light from the line emission of high concentration elements. The first of these effects can be compensated by utilizing a correction of raw data. The second effect may require selection of an alternate wavelength. The third and fourth effects can generally be compensated by a background correction adjacent to

the analyte line.

5.1.1 Spectral overlaps may be avoided by using an alternate wavelength, using multiple wavelengths for each element in your method, or can be compensated for by equations that correct for interelement contributions, which involves measuring the interfering elements. Some potential on-line spectral interferences observed for the recommended wavelengths are given in Table 3. These interferences will produce false-positive or false-negative determinations and be reported as analyte concentrations. Users may apply interelement correction factors determined on their instruments to compensate off-line or on-line for the effects of interfering elements.

5.1.2 When interelement corrections are applied, there is need to verify their accuracy by analyzing spectral interference check solutions as described in Section 8.6 . Interelement corrections will vary among instruments because of differing resolution and choice of background correction points. Interelement corrections that constitute a major portion of an emission signal may not yield accurate data. Users should remember that some samples may contain uncommon elements that could contribute spectral interferences.

5.1.3 The interference effects must be evaluated for each individual instrument and each method since intensities will vary not only with optical resolution but also with operating conditions such as power, viewing height and argon flow rate. Interelement correction factors are method specific and must be redetermined if any changes are made to the method. When using the recommended wavelengths given in Table 3, the analyst must determine and document for each wavelength the effect from the known interferences given in Table 3, and to utilize a computer routine for their automatic correction on all analyses. The location for background correction must be either free of off-line interelement spectral interference or a computer routine must be used for their automatic correction on all determinations. If a wavelength other than the recommended wavelength is used, the user must determine and document both the on-line and off-line spectral interference effect from all method analytes and provide for their automatic correction on all analyses. Tests to determine the spectral interference must be done using analyte concentrations that will adequately describe the interference. Normally, 100 mg/L single element solutions are sufficient, however, for analytes such as iron that may be found at high concentrations a more appropriate test would be to use a concentration near the upper LDR limit. See Section 8.6 for required spectral interference test criteria.

5.1.4 When interelement corrections are not used, either on-going SIC solutions

(Section 8.6) must be analyzed to verify the absence of interelement spectral interference or a computer software routine must be employed for comparing the determinative data to limits files for notifying the analyst when an interfering element is detected in the sample at a concentration that will produce either an apparent false positive concentration, greater than the analyte IDL or false negative analyte concentration, less than the 99% lower control limit of the calibration blank. When the interference accounts for 10% or more of the analyte concentration, either an alternate wavelength free of interference or another approved test procedure must be used to complete the analysis. If not using IEC corrections routinely, monitor concentrations of interfering elements and use multiple wavelengths for each method element. If an interfering element is present in amounts that will interfere with your analyte concentration then use one of the alternate wavelengths to report that analyte concentration or rerun using IEC corrections.

5.2 Physical interferences: Are generally considered to be effects associated with the sample nebulization and transport processes. These originate from differences in surface tension and/or viscosity between samples and calibrating standards. Differences in these properties due to high concentrations of dissolved solids can be particularly troublesome. Although the nebulizer/spray chamber system can accommodate high dissolve solids for short periods of time, it is advisable to keep the dissolved solids content at a level of 0.5 percent or less for routine work. The use of the peristaltic pump lessens these interferences. If these types of interferences are operative, they must be reduced by sample dilution and/or utilization of a standard additions technique such as Meyers/Tracey signal compensation. Internal standards can be utilized in an intensity ratioing procedure to compensate for the effect of an aerosol transport interference. An internal standard is an element present at the same concentration in all standards, the blank, and the samples. When a sample is run, the intensity of the internal standard element (Scandium-for ICP Meyers-Tracey) is compared with the intensity of the internal standard in the calibrating standards. If they are equivalent, then the analyte intensity in the sample is used as measured to calculate a concentration. If a physical interference has caused the intensity of the internal standard in the sample to be different from that measured in the calibrating standard, then the intensity of the analyte in the sample is automatically corrected by the ICP software. The most effective method of minimizing the effect of physical interferences is to carefully match the matrix composition of standards, samples and the blank. Also, better control of the argon flow rate improves instrument performance. For this reason the instrument uses mass flow controllers for determining the rate of flow for the argon.

5.3 Chemical interferences: Are characterized by molecular compound formation, ionization effects and solute vaporization effects. Normally these effects are not

pronounced with the ICP technique. If they are observed they can be minimized by careful selection of operating conditions, by buffering the sample, matrix matching, or standard addition procedures. These types of interferences can be highly dependent on matrix type and the specific analyte element.

5.4 The occurrence of the above mentioned interferences are primarily attributed to the sample matrix. If an interference caused by a particular matrix is known, in many cases it can be circumvented. However, when the nature of the sample is unknown, tests as outlined below can be used to assure the analyst that neither positive nor negative interference effects are operative in any of the analyte elements.

5.4.1 Serial dilution: If the analyte concentration is sufficiently high (a factor of 10X the MDL or greater after dilution), an analysis of a dilution should agree within 10% of the original determination. If not, a chemical or physical interference should be suspected.

5.4.2 Analyte addition: A post digestion analyte addition added at a minimum level of 20X the MDL (maximum 100X) to the original determination should be recovered within established control limits. If not, a matrix effect should be suspected. The use of a standard addition technique can usually compensate for this effect but the analyst should be cautioned that the standard addition technique will not detect coincident spectral overlap. If this is suspected, monitor more than one wavelength for each analyte and compare the concentrations of analyte, or the use of spectral compensation, an alternate wavelength, or comparison with an alternate method is suggested.

5.4.3 Wavelength scanning of analyte line region: Can be performed to detect potential spectral interferences.

5.5 Selection of Analyte Wavelengths: The most important parameter in the development of an analytical method is the analyte wavelength. The ICP 3000 covers the range of wavelengths 165-782 nm and has a resolution of .005-.006 nm. The items discussed below should be taken into consideration before making the selection.

5.5.1 Nature of Transition - The spectral lines observed in ICP spectroscopy originate from neutral and singly ionized forms of the elements. It is preferable to employ ion lines whenever other considerations permit as they are usually less affected by small changes in the operating conditions of the plasma. Some elements however do not exhibit ion lines of useful intensity two of which are aluminum and boron.

5.5.2 BEC and Detection Limits - Background equivalent concentration is employed in emission spectroscopy to compare the signal to background ratio of the various emission wavelengths of an element. It is defined as the concentration of the analyte that gives an emission signal that is equal to the intensity of the plasma background at the selected wavelength. The instrument manual describes how to calculate these for each wavelength. Detection limits can be determined from a BEC. A reasonable detection limit can be calculated by dividing the BEC by 10.

5.5.3 Linear Working Range - The upper limits of the linear working range for each element wavelength may vary. If the element concentrations exceed the linear working range of a wavelength it may be desirable to utilize a less sensitive wavelength.

5.5.4 Interference Equivalent Concentration - The IEC is defined as the intensity change, expressed as milligrams of analyte per liter of solution resulting from the analysis of a solution containing 1000 mg/l of an interferant at the analyte wavelength. The IEC indicates the degree of background interference to be expected at a particular wavelength for a particular matrix component. The Optima 3000 has a special program for setting up and testing IEC corrections. These values can be found in the wavelength calibration tables.

5.5.5 Memory effects - Memory interferences result when analytes in a previous sample contribute to the signals measured in a new sample. Memory effects can result from sample deposition on the uptake tubing to the nebulizer, and from the buildup of sample material in the plasma torch and spray chamber. The site where these effects occur is dependent on the element and can be minimized by flushing the system with a rinse blank between samples. The possibility of memory interferences should be recognized within an analytical run and suitable rinse times should be used to reduce them. The rinse times necessary for a particular element must be estimated prior to analysis. This may be achieved by aspirating a standard containing elements corresponding to either their LDR or a concentration ten times those usually encountered. The aspiration time should be the same as a normal sample analysis period, followed by analysis of the rinse blank at designated intervals. The length of time required to reduce analyte signals to within a factor of two of the method detection limit should be noted. Until the required rinse time is established, this method requires a rinse period of at least 60 seconds between samples and standards. If memory interference is suspected, the sample must be re-analyzed after a long rinse period. Boron exhibits memory effects above a concentration of 400 ug/L and a long rinse time is

necessary for this method analyte. Samples of higher than 400 ug/L are diluted into the range below this amount.

5.6 Wavelength Range Characteristics

5.6.1 170-190 nm Spectra Range - strong oxygen absorption bands interfere at wavelengths lower than 190 nm. Oxygen can be effectively removed from the optical path of the spectrometer, from the source to the detector by purging with argon or nitrogen which are optically transparent in this region. If the problem still exists another wavelength may be required.

5.6.2 Wavelengths longer than 190 nm.

5.6.2.1 200-260 nm - In this region nitric oxide emission bands structurally complicate the plasma background. These are thought to arise from atmospheric nitrogen becoming entrained in the plasma discharge.

5.6.2.2 280-340 nm - In this region emission bands due to the molecular species OH have been reported.

5.6.2.3 >300 nm - Fewer spectral overlaps exist in this region (except for rare earth elements).

5.6.2.4 190-310 nm - A good signal-to-noise ratio for most elements.

5.6.2.5 215-250 nm - In this range resides the most spectral overlap interferences from transition elements.

5.6.2.6 <200 nm - This is the vacuum range. There is not much spectral structure, also Meyers-Tracey does not work well.

6.0 Safety

6. 1 The toxicity or carcinogenicity of each reagent used in this method has not been fully established. Each chemical should be regarded as a potential health hazard, and exposure to these compounds should be as low as reasonably achievable through using hoods, gloves and other appropriate personal safety equipment.

6.2 Analytical plasma sources emit radio-frequency radiation and intense UV radiation. Suitable precautions should be taken to protect personnel from such hazards. The ICP instrument has numerous "interlocks" which extinguish the plasma should

hazardous conditions arise and these should never be defeated.

6.3 Precautions should also be taken to minimize other potential hazards. Basic good housekeeping and safety practices such as the use of rubber or plastic gloves, lab coat, and safety glasses during handling of samples and cleaning of labware are recommended.

6.4 This method does not address all safety issues associated with its use. The laboratory is responsible for maintaining a safe work environment and a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets (MSDS) should be available to all personnel involved with these analysis.

6.5 As with all electrical and heated instruments, observe basic safety rules. Do not touch electrical areas and allow surfaces to cool before touching.

7.0 Equipment and Supplies: Note: Brand names, suppliers, and part numbers are cited for illustrative purposes only. No endorsement is implied. Equivalent performance may be achieved using equipment and materials other than those specified here, but demonstration of equivalent performance that meets the requirements of this method is the responsibility of the laboratory.

7.1 Analytical instrumentation and supplies

7.1.1 Perkin Elmer Optima 3000DV simultaneous inductively coupled plasma-atomic emission spectrometer

7.1.2 Gateway, GP7-550

7.1.3 ICP Winlab32 software, version 2.2 October19, 2000

7.1.4 Perkin Elmer AS90 autosampler with trays

7.1.5 Neslab CFT-33 water recirculator

7.1.6 Peristaltic pump

7.1.7 Peristaltic pump tubing, solvent-flex or standard, black/black, any major supplier for sample line. Caution: solvent-flex tubing has a zinc contamination.

7.1.8 Peristaltic pump tubing, solvent-flex or standard, red/red any major supplier for waste line.

7.1.9 50 mL plastic centrifuge tubes, any major supplier.

7.1.10 15 mL plastic centrifuge tubes, any major supplier.

7.1.11 Argon gas supply, liquid gas pack, high purity grade (99.99%), local supplier Praxair 223-8255. Located in garage-pressure should be 80psi.

7.1.12 Nitrogen gas supply, liquid gas pack, local supplier Praxair 223-8255. Located in garage-pressure should be 60 psi.

7.1.13 Compressed air: Used as shear gas - pressure should be 60 psig. Connected to lab compressed air supply.

8.0 Reagents and Standards

8.1 Reagents: Reagents may contain elemental impurities which might affect analytical data. Only high-purity reagents should be used whenever possible. All acids used for this method must be of ultra high purity grade. Suitable acids are available from most major suppliers.

8.1.1 Nitric acid, concentrated

8.1.2 Water: For all sample preparation and dilutions, ASTM type I water is required. Suitable water may be prepared by passing reverse osmosis water through a mixed bed of anion and cation exchange resins. This is the water which is delivered from the "Milli-Q" water system in room 305.

8.2 Standards

8.2.1 Stock standard solutions: Purchased from a reputable commercial source such as SPEX in concentrations of 1000 ug/ml or 10000 ug/ml.

8.2.2 Mixed calibration solutions: Prepare mixed CAL solutions by combining appropriate volumes of the stock standard solutions in volumetric flasks. Add concentrated nitric acid first to a small volume of water in the flask so that the final concentration of nitric acid will be 2%. Then add the aliquots of stock standard and finally dilute to volume with ASTM type I water, according to the amounts and combinations in Table 4. Transfer the freshly prepared CAL solutions to clean polyethylene bottles for storage and label

with date, concentration and name. Fresh mixed CAL solutions should be prepared as needed with the realization that concentrations can change on aging. The CAL solutions must be initially verified using a quality control sample. Listed here are some commonly used standards.

8.2.2.1 Mixed calibration solution "cat" contains sodium, magnesium, potassium, calcium, iron, manganese, silica in the following concentrations with a final volume of 500 mL.

| Analyte | Aliquot | Stock Standard | Concentration |
|---|---|---|---|
| Na | 25 mL | 10000 mg/L | 500 mg/L |
| Mg | 5 mL | 10000 mg/L | 100 mg/L |
| K | 2.5 mL | 10000 mg/L | 50 mg/L |
| Ca | 10 mL | 10000 mg/L | 200 mg/L |
| Mn | 1.25 mL | 1000 mg/L | 2.5 mg/L |
| Fe | 1.25 mL | 1000 mg/L | 2.5 mg/L |
| SiO2 | 1.25 mL | 10000 mg/L | 53.5 mg/L |

In addition to this "#1 cat" standard above, prepare standards with concentrations of the same elements equivalent to 1:2.5 and 1:10 relative to the base "cat" standard. A 1:0.5 solution is read at the end of the run to check linearity. Also prepare a mixed calibration standard with concentrations of 10000 mg/L Sodium, 4000 mg/L Calcium, 2000 mg/L Magnesium, 1000 mg/L Potassium, 1070 mg/L Silica, 50 mg/L Iron, and 50 mg/L Manganese for spiking purposes. This is spiking solution "cat".

8.2.2.2 Mixed calibration solution for aluminum and boron made with the following concentrations with a final volume of 1000 mL.

| Analyte | Aliquot | Stock Standard | Concentration |
|---|---|---|---|
| Al | 500 uL | 1000 mg/L | 500 ug/L |
| B | 500 uL | 1000 mg/L | 500 ug/L |

8.2.2.3 Mixed calibration solution identified as both "#1 beba" and "#1 tsec" and now called “sdwa” and contains copper, beryllium, barium, nickel, aluminum, zinc and if needed silver (see below) in the following concentrations with a final volume of 500 mL.

| Analyte | Aliquot | Stock Standard | Concentration |
|---|---|---|---|
| Cu | 0.5 mL | 1000 mg/L | 1000 ug/L |
| Be | 0.5 mL | 1000 mg/L | 1000 ug/L |
| Ba | 0.5 mL | 1000 mg/L | 1000 ug/L |
| Ni | 0.5 mL | 1000 mg/L | 1000 ug/L |
| Al | 0.5 mL | 1000 mg/L | 1000 ug/L |
| Zn | 0.5 mL | 1000 mg/L | 1000 ug/L |

Because silver is not as stable in solution as the other elements it must be added to this mixture (spiked in) just before the analysis run is started. Take 50 mLs of standard and spike with 50 uL of 1000 mg/L silver stock standard. This will lead to a final concentration of 1000 ug/L. In addition to the "beba" and "tsec" standard above, prepare standards with concentrations of the same elements equivalent to 1:2.5 and 1:5 relative to the base "beba" and "tsec" standard. In addition, prepare a laboratory fortified sample matrix (LFM or "spike") with concentrations of 10000 ug/L for each element in the "beba" and "tsec" standard. This will serve as a spiking solution and will be identified as spike solution "sdwa".

8.2.2.4 Mixed calibration solution "#1 bcz" contains barium, copper, and

zinc in the following concentrations with a final volume of 500 mL.

| Analyte | Aliquot | Stock Standard | Concentration |
|---|---|---|---|
| Ba | 0.5 mL | 1000 mg/L | 1000 ug/L |
| Cu | 0.5 mL | 1000 mg/L | 1000 ug/L |
| Zn | 0.5 mL | 1000 mg/L | 1000 ug/L |

In addition to the "bcz" standard above, prepare standards with concentrations of the same elements equivalent to 1:2.5 and 1:5 relative to the base "bcz" standard. In addition, prepare a laboratory fortified sample matrix (LFM or "spike") with concentrations of 10000 ug/L for each element in the "bcz" standard. This will serve as a spiking solution and will be identified as spike solution "bcz".

8.2.2.5 Calibration solution "cu #5" contains copper in the following concentration with a final volume of 500 mL.

| Analyte | Aliquot | Stock Standard | Concentration |
|---|---|---|---|
| Cu | 2.5 mL | 1000 mg/L | 5000 ug/L |

No diluted standards are required because the "#1 bcz" standard and its 1:2.5 dilution will be used for linearity checks and the "bcz" spike solution will be used for spiking purposes.

8.2.2.6 Calibration solution "#3 feed" contains calcium, sodium, potassium and phosphorus in the following concentrations with a final volume of 200 mL.

| Analyte | Aliquot | Stock Standard | Concentration |
|---|---|---|---|
| Ca | 10 mL | 10000 mg/L | 500 mg/L |
| Na | 10 mL | 10000 mg/L | 500 mg/L |
| K | 10 mL | 10000 mg/L | 500 mg/L |
| P | 10 mL | 10000 mg/L | 500 mg/L |

8.3 Blanks: Three types of blanks are required for this method. A calibration blank is used to establish the analytical calibration curve, a laboratory reagent blank is used to assess possible contamination from the sample preparation procedure and a rinse blank is used to flush the instrument uptake system and nebulizer between standards and samples to reduce memory interferences.

8.3.1 Calibration blank: Prepare by diluting a mixture of 20 mL of conc. nitric acid to 1000 mL with ASTM type I water. Store in a plastic bottle.

8.3.2 Laboratory reagent blank: Contains all the reagents in the same volumes used in processing the samples. The LRB must be carried through the entire preparation procedure and analysis scheme. The final solution should contain the same acid concentrations as sample solutions for analysis.

8.3.3 Rinse blank: Prepare this wash solution by rinsing the zero position cup with reverse osmosis water and filling with reverse osmosis water and adding 4 ml of nitric acid.

8.4 Quality control sample: These solutions are prepared from a source external to the laboratory. Follow the instructions for preparing these solutions provided by the supplier of the samples.

8.5 Instrument Performance Check (IPC) Solution: The IPC solution should be prepared from the same standard stock solutions used to prepare the calibration standards and stored in an FEP bottle. The concentrations used are the same as the spike amounts listed in Table A except Ag should be < 0.5 mg/L and K, P, and Silica should be 10 mg/L and all others 2 mg/L.

8.6 Spectral interference check (SIC) solution: Purchased from a reputable supplier.

Follow the instructions provided for preparing and analyzing the interference check solution. May be prepared from stock standard solutions in appropriate concentrations. When interelement corrections are applied, SIC solutions are needed containing concentrations of the interfering elements at levels that will provide an adequate test of the correction factors..

8.6.1 SIC solutions containing Fe 300mg/L, Al 200mg/L, Ba, Be, Cd, Ce, Co, Cr, Cu, Mn, Mo, Ni, Sn, SiO2, Ti, Tl, V all 50 mg/L should be prepared in the same acid mixture as the standards and stored in FEP bottles. These solutions can be used to periodically verify a partial list of the on-line and possible off-line interelement spectral correction factors for the recommended wavelengths given in Table 3. Multielement SIC solutions may be prepared and substituted for the single element solutions provided an analyte is not subject to interference from more than one interferant in the solution. Note: If wavelengths other than those recommended in Table 3 are used, other solutions different from those above may be required.

8.6.2 For interferences from iron and aluminum, only those correction factors when multiplied by 100 to calculate apparent analyte concentrations that exceed the determined analyte IDL or fall below the lower 3-sigma control limit of the calibration blank need be tested on a daily basis.

8.6.3 For the other interfering elements, only those correction factors when multiplied by 10 to calculate apparent analyte concentrations that exceed the determined analyte IDL or fall below the lower 3-sigma control limit of the calibration blank need be tested on a daily basis.

8.6.4 If the correction routine is operating properly, the determined apparent analyte concentration from analysis of each interference solution should fall within a specific concentration range bracketing the calibration blank. This concentration range is calculated by multiplying the concentration of the interfering element by the value of the correction factor being tested and dividing by 10. If after subtraction of the calibration blank the apparent analyte concentration is outside this range, a change in the correction factor of more than 10% should be suspected. The cause of the change should be determined and corrected and the correction factor should be updated. Note: The SIC solution should be analyzed more than once to confirm a change has occurred with adequate rinse time between solutions and before subsequent analysis of the calibration blank.

8.6.5 If the correction factors tested on a daily basis are found to be within the 10% criteria for 5 consecutive days the required verification frequency of those

factors in compliance may be extended to a weekly basis. Also, if the nature of the samples analyzed is such ( e. g. finished drinking water) that they do not contain concentrations of the interfering elements at the 10 mg/L level, daily verification is not required; however, all interelement spectral correction factors must be verified annually and updated, if necessary. Infrequently used interelement spectral correction factors are always verified each time they are used.

8.6.6 For instruments without interelement correction capability or when interelement corrections are not used, SIC solutions (containing similar concentrations of the major components in the samples, >10 mg/L) can serve to verify the absence of effects at the wavelengths selected. These data must be kept on file with the sample analysis data. If the SIC solution confirms an operative interference that is > 10% of the analyte concentration, the analyte must be determined using a wavelength and background correction location free of the interference or by another approved test procedure. Users are advised that high salt concentrations can cause analyte signal suppressions and confuse interference tests.

9.0 Sample Collection, Preservation, and Storage

9.1 For determination of dissolved elements, the sample must be filtered through a 0.45 um membrane filter. Use a portion of the filtered sample to rinse the filter flask, discard this portion and collect the required volume of filtrate. Acidify the filtrate with nitric acid immediately following filtration to pH < 2.

9.2 For the determination of total recoverable elements in aqueous samples, acidify with nitric acid at the time of collection to pH < 2. The sample should not be filtered prior to digestion. Samples that cannot be acid preserved at the time of collection because of sampling limitations or transport restrictions should be acidified with nitric acid to pH < 2 upon receipt in the laboratory. Following acidification, the sample should be held for 24 hours before withdrawing an aliquot for sample processing. Digest according to Method I-1-32 .

9.3 Solid samples require no preservation prior to analysis other than storage at 4$^{o}$C.

9.4 All metal samples are stored at room temperature in Room 305 or storage room.

10.0 Quality Assurance/Quality Control

10.1 <u>An LRB (reagent blank) and calibration blank</u> shall be analyzed in each run.

10.2 Spike and duplicate 10% of all samples analyzed with a minimum of one spike and one duplicate per run. Analyze a spiked blank (lab fortified blank) in each run.

10.3 Laboratory fortified sample matrix (LFM or "Spike"): See section 10.10. Recovery calculations are not required if the concentration added is less than 10% of the background concentration. If recovery of any analyte falls outside the designated range and laboratory performance for that analyte is shown to be in control (Laboratory performance checks are within specified range), the recovery problem encountered with the fortified sample is judged to be matrix related. The data user should be informed that the result for that analyte in the unfortified sample is suspect due to matrix effects and analysis by method of standard addition should be considered.

10.4 Duplicate data. Duplicates should be studied and for most samples duplicates should fall within 10% of each other. It is suggested that the analysts use their judgement in the evaluation of the duplicate data.

10.5 Linearity check. The standards read at the end of each run should all read within 10% of their actual concentration. The analysts should also use their experience in interpreting the linearity data.

10.6 Laboratory performance check-IPC. The values for the laboratory performance checks must fall within the allowable range for each analyte in each performance check used. Recovered analyte concentrations of this sample must be within acceptable limits or samples must be rerun.

10.7 If the analytical run is suspect due to any of the previous four points, the samples from the section of the analytical run which was determined to be out of control must be rerun following recalibration.

10.8 Initial Demonstration of performance.

10.8.1 An MDL shall be established for each analyte using reagent water (blank) fortified at a concentration of two to five times the estimated detection limit. To determine MDL values, take seven replicate aliquots of the fortified reagent water and process through the entire analytical method. Perform all calculations defined in the method and report the concentration values in the appropriate units. Calculate the MDL as follows:

$$MDL = (t) \times (S)$$

where: t = value for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom is, t =

3.14 for seven replicates.
S = standard deviation of the replicate analysis.

10.8.2 An MDL shall be determined annually or whenever a significant change in background or instrument response is expected and documented.

10.8.3 Linear calibration ranges: The upper limit of the linear calibration range shall be established for each analyte by determining the signal responses from a minimum of three different concentration standards, one of which is close to the upper limit of the linear range. Linear calibration ranges shall be determined annually or whenever a significant change in instrument response is observed.

10.8.4 Quality control sample (QCS): When beginning the use of this method, on a quarterly basis, after purchasing new stock or preparing new calibration standard solutions verify the calibration standards and acceptable instrument performance with the preparation and analysis of a quality control sample. To verify the calibration standards the determined mean concentrations from 3 analyses of the QCS must be within ± 5% of the stated values. If the calibration standard cannot be verified, performance of the determinative step of the method is unacceptable. The source of the problem must be identified and corrected before either proceeding on with the initial determination of method detection limits or continuing with on-going analyses.

10.9 Assessing Laboratory Performance: Reagent and fortified blank

10.9.1 The laboratory must analyze at least one LRB with each set of samples. LRB data are used to assess contamination from the laboratory environment and to characterize spectral background from the reagents used in sample preparation. If an analyte value in an LRB exceeds its determined MDL, then laboratory or reagent contamination is suspected. Any determined source of contamination should be eliminated and the samples reanalyzed.

10.9.2 One LFB (spiked blank) must be analyzed with each batch of samples. Calculate accuracy as percent recovery. If recovery of an analyte falls outside control limits of 85-115%, the method is judged out of control. The source of the problem should be identified and resolved before continuing the analysis.

10.9.3 Instrument performance check (IPC) solution - For all determinations the laboratory must analyze the IPC solution and a calibration blank immediately following daily calibration, after every tenth sample and at the end of the

sample run. Analysis of the calibration blank should always be less than the analyte IDL, but greater than the lower 3-sigma control limit of the calibration blank. Analysis of the IPC solution immediately following calibration must verify that the instrument is within plus or minus 5% of calibration. Subsequent analysis of the IPC solution must be within plus or minus 10% of calibration. If the calibration cannot be verified within the specified limits, reanalyze either or both the IPC solution and calibration blank . If the second analysis of the IPC solution or the calibration blank confirm calibration to be outside the limits, sample analysis must be discontinued, the cause determined, corrected and /or the instrument recalibrated. All samples following the last acceptable IPC solution must be reanalyzed. The analysis data of the calibration blank and IPC solution must be kept on file with the sample analysis data.

10.9.4 Spectral interference check (SIC) solution: For all determinations the laboratory must periodically verify the interelement spectral interference correction routine by analyzing SIC solutions. See section 8.6 for preparation and concentration directions and on-going verification routines.

10.10 Assessing analyte recovery: Laboratory fortified sample matrix (spiked samples)

10.10.1 Spike 10% of samples or at least one per run. Select a representative water sample of the type of samples being analyzed. It is recommended that this sample be analyzed prior to fortification. The spike amount should be 20% to 50% higher than the analyzed value. Over time, samples from all routine sample sources should be fortified.

10.10.2 Calculate the percent recovery, corrected for background concentrations measured in the unfortified sample, and compare these values to the control limits of 70-130% A recovery calculation is not required if the concentration of the analyte added is less than 30% of the sample background concentration. Percent recovery may be calculated in units appropriate to the matrix, using the following equation:

$$R = \frac{Cs - C}{s} \times 100$$

where, R = percent recovery
Cs = fortified sample concentration
C = sample background concentration

s = concentration equivalent of fortifier added to water sample.

10.10.3 If analyte recovery falls outside the designated range, and the laboratory performance is shown to be in control see section 10.9, the recovery problem encountered with the spiked water sample is judged to be matrix related, not system related. The result for each analyte in the unspiked sample must be labeled to inform the data user that the results are suspect due to matrix effects.

11.0 Calibration and Standardization

11.1 Specific wavelengths are listed in Table 2. Other wavelengths may be substituted if they can provide the needed sensitivity and are corrected for spectral interference. Instrument operating conditions vary with different analytes but must be capable of providing data of acceptable quality to the data user. Operating conditions vary from 1300-1500 watts power, 9-18mm viewing height, 15liters /min argon plasma flow, aux argon flow 0.3-0.5 L/min, neb flow 0.50-0.90 L/min depending on method used and orientation of the torch, radial or axial. Axial needs a more robust plasma with higher power and lower neb flow and more attention to interferences. Axial conditions and methods are in the developmental stage and will be added as finished. All conditions are method specific and are computer controlled once specified in the method.

11.2 Typically three standards and a calibration blank are used. See section 8.2 for preparation instructions and further information.

11.3 Before calibrating, instrument must be started and warmed up according to instructions in the following procedure section.

11.4 Instrument has a calibration routine and will form the calibration curve. The calibration curve should be checked before reading any samples to be sure it is within acceptable range of at least .99 or better depending on which analyte is being tested. The calibration data is automatically printed with instrument data after calibration is complete.

12.0 Procedures

12.1 Instrument startup and warmup procedures

12.1.1 Interlocks:

12.1.1.1 The following interlocks must be satisfied in order to ignite the plasma. If any of these interlocks are interrupted while the plasma is on, the plasma will automatically be shut down. The front and side doors on the sample compartment must be closed before you can ignite the plasma. Argon pressures for the torch must be correct. Argon pressure leaving the tank must at least 80 psi. Cooling water must be flowing to the RF coil.

12.1.1.2 The following interlocks are for the detectors. If any of these are interrupted while the system is operating, the detectors will be shut down. The argon purge for the detectors monitored by flow switches, must be functioning properly. Nitrogen purge for the spectrometer optics should be on to protect the optics but is not required to run. The instrument can operate without nitrogen gas but be consistent within each run. The temperature of the optics housing must be 36-40° C. The temperature of the detector must be less than -30° C. The purge gas, compressed air, must be on and at correct pressure (60 psi).

12.1.2 Initialization Steps (see page 2-20 of the Optima 3000 Hardware Guide for a detailed description)

12.1.2.1 The main power switch is used to turn on the spectrometer (and is normally left on). When the switch is first turned on, a system clock checks to see how long the instrument has been off. Based on this time, the system determines what startup routines must be carried out before the instrument can be operated and displays the wait time on the computer (13 to 73 minutes). The software sends instructions to the instrument for the required initialization sequence. If the software is not on initially or any time the argon tank is changed, the instrument software must be reinitialized or restarted manually for this routine to take effect.

12.1.2.2 The RF generator, which is switched on by the RF Generator standby switch, takes about ten minutes to warm up. This switch should be turned off at the end of the day but must be switched on before the computer is turned on. Once the plasma has been ignited, you should wait one hour for the system to stabilize before running samples.

12.1.3 The computer is on at all times but instrument software is closed at the end of each day and is completely rebooted at the start of each day. Windows will load first. Press enter when prompted for password. The lms can be accessed from the instrument computer. Make worklist as per instructions in section 12.2.

12.1.4 Check water, air, argon and nitrogen. Open door to check torch and all tubing. Close door. Click on Optima icon to access winlab software.

12.1.5 Prepare the instrument for warmup: Rinse and fill the 250 mL plastic beaker in position 0 of the autosampler with RO water containing 4 mL of nitric acid, replace the peristaltic pump tubing for the pump drain with red/red tubing, and replace the peristaltic pump tubing for the sample introduction system with black/black tubing. Make sure that the sample tube on autosampler is in the down position and tip is in water in rinse cup. Close latches on pump making sure tubes are positioned properly. The green system ready light on front of instrument should be lit.

12.1.6 Ignite the plasma: Click on plasma control. When all interlocks are ready, click the plasma switch to on. At all times while the plasma is igniting watch for strange discharge behavior and extinguish the plasma immediately if such behavior is observed by clicking on the off button or pressing the red emergency plasma off button on front of instrument. The ignition process requires approximately 75 seconds and can be monitored by messages in lower left corner. The pump automatically shuts off at the beginning of the ignition sequence and is restarted at the end of the ignition sequence. A successful ignition is indicated by the yellow Plasma On light on the front of the instrument. If problems are encountered in achieving a successful ignition see chapter 2-18 of the Winlab software guide. The most probable cause of problems is the ignitor, check to see the cable is attached and fittings are tight. If the plasma will still not ignite, contact the supervisor. After a successful ignition allow the instrument to warm-up for at least one hour.

12.1.7 During or after the instrument warm-up period but before starting any analysis do a mercury realign. Click on Tools, Spectroscopy Control, Hg Realign button. Do at least once daily or as often as needed. Click on System, Diagnostics, Update- print out UV and VIS temperature, and Hg realign cps and save in drawer. At least monthly or anytime needed, an align view both axial and radial, using a manganese solution, is performed to make sure that the torch is aligned correctly.

12.1.8 While instrument is warming up enter data needed for an analysis:

Open automated analysis window and with setup button highlighted, Click on method and select correct method like cationsSio2 . See file containing copies of updated methods and check that standards are correct and in correct autosampler location. Click on SIF and open correct SIF like cat1. See section 12.2. Make sure SIF has been modified and everything is correct and ready for analysis and saved. Click on results data set name and enter name which is usually the date and SIF name (like 030303cat1). Click on print log. Save data should be marked. If you wish to have the plasma automatically extinguish itself after run is completed, set date and time off or turn off at completion of run in Automatic Shutdown. Highlight wash options, 30 min and shutdown options, turn off plasma and pump. All windows needed for running a specific method can be saved as a workspace and recalled each time that method is run by clicking on the workspace name, such as cat1.

. 12.2 Creating a sample queue

12.2.1 Make worklist as usual. Log onto lims and pick 1. Enter analyst number.

12.2.2 Select 3 (create/fill/distribute worklists). Select create. Choose a worklist from the table below:

| To run... | Choose Worklist | Use sif | Use method |
|---|---|---|---|
| | | | |
| Na, Mg, K, Ca, Mn, Fe,Sio2 | secsi | cat1,2,3 | cationsio2rep |
| TCLP | tclp | tclp,tclp1 | tclpplus |
| Al, B (1113,1105) | alb | alb | alb |
| Al,B,Fe,Mndiss (1713,1705) | albdiss | albdiss | albfemn |
| Pb in paint | 1682 | pbpaint | Pb in paint |
| For Li,Sr,Al,Ti,B | ICP5 | any | lisrtial |
| To create any | ICP? (1-6) | any | appropriate |
| Na, Mg, K, Ca, Mn, Fe, | sec | cat1,2,3 | cations |
| Al as diss Al | al | al | DissAl |

| | | | |
|---|---|---|---|
| SiO2 | sio2 | sio2,sio2- | sio2 |
| Cu in Pb/Cu | cu | cu1,2,3 | Cu |
| Cu,Be, Ba, Ni in SDWA | beba | sdwa4 | sdwa_iec4 |
| Al, Zn, Ag in SDWA | tsec | | tsec? |
| Ba, Cu, Zn | bcz | bcz, 1,2,3 | BCZsoils |
| Large group of metals | ? | nawqa, 2 | NAWQA |
| | | | |

Choose the number of samples you wish to run (<80), and select instrument export. When prompted for a file refer to the table above, pick the SIF for your method (e. g. a file name like cat1). If any errors are received, repeat the export process to insure that the log numbers have transferred. Repeat for desired worklists and exit lims.

12.2.3 At desktop, click on Make SIF. Type in SIF name you transferred from lims. Go back to optima software.

12.2.4 Edit the SIF which you exported to the ICP. This involves clicking on file, open, Sample Info File, Type in name or highlight name from the list of the SIF you exported. Check autosampler positions and log numbers and change if needed to reflect where you will actually be placing the samples. Add QC numbers from method you are using in the Analyze QC's Before column. Check that info in Matrix Check Samples column is correct. Enter any dilution info in columns Aliquot Volume and Diluted To Vol. Save. Minimize. In Automated Analysis Control window click on analyze. Now open Analysis Sequence window and check that all info is correct for method you are running. Print. Use this list to fill your autosampler tray. If you need to change any info in the SIF file you will need to save it and then go back to the set up window and then to the analyze window in order to use it in the analysis. Always click on rebuild list just before starting to be sure all changes are incorporated into your files for that analysis.

12.2.5 Fill the autosampler tray. This involves placing 50 and 15 mL centrifuge tubes to hold the standards, checks and samples respectively. Label the tubes with sample log numbers and standard identifications. Check the conductivities of the samples which you will be analyzing. If needed perform dilutions on the samples according to the following table.

| Conductivity, umhos/cm | Dilution Factor |
|---|---|
| < 5000 | 1:1 |
| 5000 - 10000 | 1:5 |
| 10000 - 20000 | 1:10 |
| 20000 - 50000 | 1:20 |
| > 50000 | See supervisor |

Be sure to edit the SIF to reflect any dilutions performed. Fill the 50 mL tubes in the autosampler tray with the proper standards, qc checks and diluted standards which correspond to the method you are running. Fill the 15 mL tubes in the autosampler tray with the samples whose log numbers are indicated on them. To the samples identified as "spike" add to 10 mL of a random sample from the run the amount of spiking standard listed in Table 1. Also choose a random sample from the run to place into the duplicate location. You should be cautioned that if you needed to do a dilution on an original sample of a spike or duplicate, remember to perform that same dilution on the spike or duplicate sample.

12.3 Analyzing the samples

12.3.1 Place the samples in the autosampler tray onto the autosampler and begin the analysis. Double check that all info in analytical sequence is correct especially log numbers, autosampler positions and any dilutions made. Begin the analysis by clicking on Analyze All to calibrate and run samples in the order in the analytical sequence. Windows open at this time include Automated Analysis Control, results, spectra, and analytical sequence. Check the calibration curve to be sure the correlation coeffiecent is greater than 0.99 but 0.999 or better is best or a recalibration is needed. Record emission counts for standards in the book on top of the ICP and check that these counts are near those of the last time method was used.

12.3.2 Periodically check the analysis run to ensure that the quality control is within acceptable limits. This involves looking at the calibration check samples, the duplicate differences, the laboratory fortified sample matrix (LFM or "spike") and LFB recoveries, the baseline, the IPC, the SIC solutions, blanks, and the calibration linearity checks.

12.3.3 If you would prefer not to use the sample queues generated by the LIMs

system it is suggested that you use the following pattern to set up your analysis method. Analyze the calibration blank followed by the calibration standards (CAL). Next analyze the instrument performance check sample (IPC) and calibration blank to insure that you have successfully calibrated the instrument. Follow this with a maximum of 10 samples, a laboratory fortified sample matrix (LFM or "spike") and a duplicate and a (LFB) laboratory fortified blank. The spike and the duplicate should be from that batch of 10 samples. Follow these with the IPC again and finally with a baseline check. It is strongly suggested that if you have more than 10 samples to analyze that you repeat the above pattern starting with the analysis of the calibration blank and ending with the baseline check. It may not be necessary to recalibrate after each batch of ten samples. This is determined by calibration checks, qc, etc...

12.3.4 After all samples have been analyzed and the final baseline check has been analyzed, analyze the calib blank and the calibration standards as samples to insure that the analysis was taking place within the linear working range of the analytes analyzed.

12.4 Instrument shutdown

12.4.1 Bring up plasma control and click to off.

12.4.2 Lift autosampler arm up. Speed up pump to empty tubing. Turn off pump.

12.4.3 Release pump tubing and loosen.

12.4.4 Exit Winlab software

12.4.5 To exit windows, click on start, click on shutdown. When safe to turn off comes up, turn off computer at switch. Turn on again, wait for screen that requests a password. Enter. Leave screen at desktop.

12.4.6 Turn off monitor.

12.4.7 Turn off RF generator.

12.5 Data reduction and reporting

12.5.1 All aluminum(396.153) and boron(249.772) analyses must be corrected for interferences from calcium and iron. The method is run as usual, making sure that sic solutions containing 1000 mg/l Ca and 100 mg/l Fe are run with other

samples. Also a mixture of 1000 mg/l Ca, 100 mg/l Fe and 200 ug/l each of Al and B is run, to be used to check iec corrections. After method is completed, go to reprocess screen, select correct data file. Select iec model builder and follow directions for making an iec correction file. Select analytes, ca and fe and wavelengths used in method. Go to corrections list and select only non zero numbers. Save as file using the date and print out factors to store with results. Go to method and select iec correction and name of iec file. After checking that iec corrections are valid, reprocess data with iec corrections. Be sure to print out reprocessed data and store with original data. Check that reprocessed data agrees with original data before entering that data. The iec correction file is specific for that day and method.

12.5.2 Open Data Manager. Highlight correct results data set from run you wish to transfer to lims. Click on export. Use existing design. Select correct design for your method usually cation or albcat. Check that design is correct for your method, check that correct sample log numbers are in the file, and analytes and wavelengths are the ones you want to transfer and will agree with lims worklist. Go to end of design and click on export data to complete transfer. Remember the name of file that data was transferred to. If you do not click on export data, data will not be transferred. Data is transferred to a report file.

12.5.3 At desktop, click on reports. Select correct file that data was transferred to. Highlight file name and with right mouse button transfer file by using send to legacy report. (A holding place for files before transferring to lims.)

12.5.4 Transfer to lims: Select lims to log on. Select 1. Enter analyst number. Select instrument, import. When prompted for the data file to import enter the name of the SIF file you saved in 12.5.2. Watch for any errors which may occur in the transfer of the data. If for some reason the transfer does not take place, you will need to manually enter the data from the raw data which was printed out on the ICP printer. Follow normal procedure if this is the case.

12.5.5 Default to report the results of the transfer to the screen. Check that correct results were transferred and enter the date and time from the raw data output. Continue from this screen and visually confirm that the data transferred accurately. Enter any true values for check samples and spikes. If there are errors, edit the log numbers or data accordingly. Distribute the worklist and complete. Exit the lims. Save LIMS printout and store with instrument data

12.5.6 Quarterly, transfer data files to the front and notify Mike Borr that it has been

sent so he can copy the file onto a tape where ICP instrument data is stored and saved. Then copy user1 result to a new user result file to save until you are sure that file has been saved on tape. Then in explore delete user1 result, remake user1 result. In Data Manager, create a new result file in user1, so that periodically you begin a new user1 result file. Allowing the files to become too large slows down the instrument and may interfere with instrument operation.

13.0 Data Analysis, Calculations, and Reporting Results

13.1 All calculations are performed by the instrument computer. Most data is electronically transferred to the LIMS system, with the analyst being responsible for verifying that the correct data was transferred. Do not report analyte concentrations below the IDL. Report data in units appropriate for your analyte number.

13.2 If a dilution factor was entered into the method, the ICP computer will calculate and print the corrected concentration. If a weight to volume factor was used it would also correct the analyzed data for this factor. The following is an example of this correction:

Dilution factor 1:20, weight to volume 5g/250mL

RawData X DilutFactor / WeightVol = Result
Raw Data X 20 / (5/0.250) = Result

13.3 Records: All raw data shall be maintained either in the laboratory facility or in a suitable storage location for a period of time not less than 10 years and since the last on site audit from the Environmental Protection Agency, whichever is longer. All raw data and the distribution printouts shall be kept in the ICP data drawers located in room 305.

14.0 Method Performance

14.1 Listed in Table 3 are the total recoverable MDLs determined for the wavelengths used, using typical operating conditions for each method on the Optima 3000 DV. The MDLs were determined using 7 replicates in reagent blank matrix. See Section 10.8.1 for complete procedure for determining MDLs.

14.2 Listed in Table A are percent recovery and standard deviation for a matrix spike, mean and standard deviation for percent recovery and result for a lab fortified blank, and mean and standard deviation for error, percent error, result, percent recovery for a known sample. All tables list number of records used for determining data.

15.0 Pollution Prevention

15.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation such as ordering smaller quantities of standards or preparing reagents in smaller amounts that can be used completely. When wastes cannot be feasiblely reduced at the source, the Agency recommends recycling as the next best option.

15.2 For information about pollution prevention that may be applicable to laboratories consult *Less is Better: Laboratory Chemical Management for Waste Reduction,* available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street N. W. , Washington D.C. 20036, 202-872-4477.

16.0 Waste Management

16.1 The Environmental Protection Agency requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations. The Agency urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions.

16.2 For further information on waste management consult *The Waste Management Manual for Laboratory Personnel,* available from the American Chemical Society at the address listed in the Section 15.2.

17.0 References

17.1 Methods for the Determination of Metals in Environmental Samples, Supplement 1, EPA Method 200.7, Revision 4.4 May 1994

17.2 Test Methods for Evaluating Solid Waste, Volume 1A, EPA Method 6010B, Revision 2, December 1996

17.3 Optima 3000 Hardware Guide and Software Guide, Perkin-Elmer Corporation, 1993

Table A

| **Element** | **Matrix** | **Spike** | Amt of | # of | **LFB** | Error | % Error | Result | %Recovery | # of |
|---|---|---|---|---|---|---|---|---|---|---|
| | %Recovery | SD | spike | Records | **TV** | SD | SD | Mean/SD | Mean/SD | Records |
| **Na** | 97.16 | 8.25 | 200 mg/L | 66 | 200 | 8.3 | 4.15 | 210/8.3 | 104.88/4.15 | 64 |
| **Mg** | 95.41 | 8.39 | 40.0 | 66 | 40 | 1.8 | 4.40 | 41.8/1.8 | 104.61/4.40 | 60 |
| **Ca** | 94.57 | 8.10 | 80.0 | 66 | 80 | 3.23 | 4.04 | 83.0/3.23 | 103.78/4.04 | 65 |
| **K** | 98.52 | 6.41 | 20.0 | 66 | 20 | 0.8 | 4.10 | 21.1/0.8 | 105.57/4.10 | 63 |
| **Fe** | 98.91 | 7.56 | 1.00 | 59 | 1 | .042 | 4.19 | 1.06/.042 | 106.46/4.19 | 64 |
| **Mn** | 95.02 | 7.82 | 1.00 | 61 | 1 | .043 | 4.34 | 1.06/.043 | 105.64/4.34 | 63 |
| **SiO2** | 98.98 | 8.35 | 21.4 | 51 | 21.3 | 1.35 | 6.30 | 22.8/1.35 | 106.7/6.3 | 62 |
| **Cd** | 88.55 | 5.85 | 4.00 | 31 | 4 | .205 | 5.12 | 4.40/.205 | 109.89/5.12 | 49 |
| **Ba** | 89.46 | 5.89 | 20.0 | 31 | 20 | .911 | 4.56 | 21.5/.911 | 107.69/4.56 | 49 |
| **Se** | 95.68 | 7.57 | 4.00 | 31 | 4 | .22 | 5.69 | 4.38/.227 | 109.39/5.69 | 49 |
| **Cr** | 89.28 | 5.63 | 4.00 | 31 | 4 | .197 | 4.92 | 4.32/.197 | 108.06/4.92 | 49 |
| **Ag** | 79.09 | 7.34 | 4.00 | 29 | 4 | .203 | 5.07 | 4.36/.203 | 109.01/5.07 | 47 |
| **As** | 91.11 | 8.67 | 4.00 | 31 | 4 | .207 | 5.18 | 4.26/.207 | 106.61/5.18 | 49 |
| **Pb** | 88.48 | 6.22 | 20.0 | 31 | 20 | .980 | 4.90 | 21.5/.980 | 107.47/4.90 | 49 |
| **Al** | 94.68 | 12.41 | 200 ug/L | 64 | 200 | 11 | 5.17 | 220/4. | 103.13/5.17 | 87 |
| **B** | 94.91 | 7.25 | 200 ug/L | 74 | 200 | 16 | 7.40 | 208/34 | 97.18/7.40 | 94 |
| | | | | | | | | | | |
| | | | | | | | | | | |
| | | | | | | | | | | |

| Element | Error | | % Error | | Result | | %Recovery | | # of | Known |
|---|---|---|---|---|---|---|---|---|---|---|
| | Mean | SD | Mean | SD | Mean | SD | Mean | SD | Records | |
| **Na** | -.05 | 1.4 | -1.32 | 3.46 | 39.5 | 1.4 | 98.68 | 3.46 | 63 | **1188** |
| **Mg** | 0.0 | 0.4 | -.12 | 3.79 | 10.0 | 0.4 | 99.88 | 6.79 | 64 | |
| **Ca** | 1.18 | 1.28 | 2.95 | 3.20 | 41.2 | 1.28 | 102.95 | 3.20 | 64 | |
| **K** | 0.2 | 0.4 | 2.38 | 4.08 | 10.2 | 0.4 | 102.38 | 4.08 | 63 | |
| **Fe** | .093 | .07 | 9.31 | 7.00 | 1.09 | .070 | 109.31 | 7.00 | 57 | **QC-** |
| **Mn** | .110 | .072 | 10.98 | 7.23 | 1.11 | .072 | 110.98 | 7.23 | 57 | |
| **SiO2** | 2.96 | 1.02 | 12.63 | 4.35 | 26.4 | 1.05 | 112.63 | 4.35 | 51 | **T143** |
| **Cd** | .019 | .035 | 1.85 | 3.48 | 1.02 | .035 | 101.86 | 3.48 | 42 | **tclp2** |
| **Ba** | .145 | .347 | 1.45 | 3.47 | 10.1 | .347 | 101.45 | 3.47 | 42 | |
| **Se** | .019 | .039 | 187 | 3.86 | 1.02 | .039 | 101.87 | 3.86 | 42 | |
| **Cr** | .018 | .035 | 1.80 | 3.47 | 1.02 | .035 | 101.80 | 3.47 | 42 | |
| **Ag** | .018 | .040 | 1.82 | 3.98 | 1.02 | .040 | 101.82 | 3.98 | 42 | |
| **As** | .000 | .045 | .02 | 4.48 | 1.00 | .045 | 100.02 | 4.48 | 42 | |
| **Pb** | .136 | .355 | 1.36 | 3.55 | 10.1 | .355 | 101.36 | 3.55 | 42 | |
| **Al** | 20 | 12 | 10.05 | 6.15 | 219 | 18 | 110.05 | 6.15 | 85 | **qc-7a** |
| **B** | 28 | 22 | 14.09 | 11.06 | 227 | 25 | 114.09 | 11.06 | 92 | |
| | | | | | | | | | | |
| | | | | | | | | | | |

Table 1. ICP Method Operating Parameters

| Method Name | Power, Watts | Nebul, mL/Min | Aux, mL/Min | Plasma, L/Min | Read Delay | View Height | Equil. Time, S | Replicates | Spike Amt |
|---|---|---|---|---|---|---|---|---|---|
| alb | 1300 | 0.85 | 0.5 | 15 | 20 sec | 15 | 15 | 3 | 200 uL bcz |
| albfemn | 1300 | 0.85 | 0.5 | 15 | 20 sec | 15 | 15 | 3 | 200 ul bcz |
| cationsio2rep | 1500 | 0.85 | 0.3 | 15 | 20 sec | 15 | 15 | 3 | 200 ul cat |
| BCZsoils | 1300 | 0.75 | 0.5 | 15 | 20 sec | 12 | 15 | 3 | 500 ul bcz |
| Cu1 | 1300 | 0.80 | 0.5 | 15 | 20 sec | 15 | 15 | 3 | 200 ul bcz |
| DissAl | 1300 | 0.85 | 0.5 | 15 | 20 sec | 15 | 15 | 3 | 250 ul bcz |
| lisrtial | 1300 | 0.85 | 0.5 | 15 | 20 sec | 15 | 15 | 3 | 250 ul bcz |
| Pb in paint | 1300 | 0.80 | 0.5 | 15 | 20 sec | 15 | 15 | 3 | 40 ul stock Pb |
| sdwa | 1300 | 0.80 | 0.5 | 15 | 20 sec | 14 | 15 | 3 | 250 ul bcz |
| sdwa_iec4 | 1300 | 0.80 | 0.5 | 15 | 20 sec | 14 | 15 | 3 | 250 ul bcz |
| tclpplus | 1300 | 0.75 | 0.5 | 15 | 20 sec | 10 | 15 | 3 | 40 ul spk soln |
| NAWQA | 1300 | 0.80 | 0.5 | 15 | 20 sec | 15 | 15 | 3 | |
| ar | 1300 | 1.00 | 0.5 | 15 | 20 sec | 15 | 15 | 3 | |
| albfemn | 1300 | 0.85 | 0.5 | 15 | 20 sec | 15 | 15 | 3 | |
| uv | 1300 | 0.85 | 0.5 | 15 | 20 sec | 15 | 15 | 3 | |

Table 2. ICP Method Parameters

| Method Name | Analytes & analyte # | Wavelength | Std Units / Sample Units | Concentration of stds | Linear Range | Report DL | Precision |
|---|---|---|---|---|---|---|---|
| al | Al_{1713} | 396.152 | ug/L \| ug/L | | > 5000 ug/L | 50 ug/L | 5.17 |
| alb | Al_{1113} | 396.152 | ug/L \| ug/L | 100-500-1000-5000 | > 5000 ug/L | 50 ug/L | 5.17 |
| | B_{1105} | 249.773 | ug/L \| ug/L | 100-200-400 | 1000 ug/L | 50ug/L | 7.4 |
| | B | 208.956 | ug/L \| ug/L | | 1000 ug/L | 50ug/L | |
| BCZsoils | Ba_{1156} | 455.409 | ug/L \| ug/L | 100-1000-5000 | > 5000 ug/L | 0.1 ug/L | 9.29 |
| | Cu_{1129} | 324.759 | ug/L \| ug/L | | > 5000 ug/L | 14 ug/L | 7.46 |
| | Zn_{1130} | 213.857 | ug/L \| ug/L | | > 5000 ug/L | 9 ug/L | 6.69 |
| sdwa_iec4 | Cu_{1129} | 324.759 | ug/L \| ug/L | 200-1000 | > 5000 ug/L | 14 ug/L | 8.38 |
| | Ni-{1128} | 231.605 | ug/L \| ug/L | | > 5000 ug/L | 20 ug/L | |
| | Be_{1104} | 313.040 | ug/L \| ug/L | | > 5000 ug/L | 0.3 ug/L | |
| | Ba_{1156} | 455.409 | ug/L \| ug/L | | > 5000 ug/L | 0.1 ug/L | |
| cationsio2rep | Na_{1211} | 589.598 | mg/L \| mg/L | 500-200-50 | >1000 mg/L | 3 mg/L | 4.15 |
| | Mg_{1212} | 279.077 | mg/L \| mg/L | 100-40-10 | >200 mg/L | 1 mg/L | 4.40 |
| | K_{1219} | 766.494 | mg/L \| mg/L | 50-20-5 | >100 mg/L | 1 mg/L | 4.10 |
| | Ca_{1220} | 317.929 | mg/L \| mg/L | 200-80-20 | >400 mg/L | 2 mg/L | 4.04 |
| | Mn_{1225} | 257.608 | mg/L \| mg/L | 2.5-1-.25 | >50 mg/L | 0.01 mg/L | 4.34 |
| | Fe_{1226} | 238.201 | mg/L \| mg/L | 2.5-1-.25 | >100 mg/L | 0.01 mg/L | 4.19 |

| Method Name | Analytes & analyte # | Wavelength | Std Units / Sample Units | Concentration of stds | Linear Range | Report DL | Precision |
|---|---|---|---|---|---|---|---|
| | Sio2_{1214 | 251.610 | mg/L \| mg/L | 53.1-21.4-10.6 | >106.2 mg/L | 2 mg/L | 6.3 |
| lisrtial | Li_{1103} | 670.788 | ug/L \| ug/L | 200-100 | > 1000 ugL | | |
| | Sr_{1138} | 407.767 | ug/L \| ug/L | 200-100-1000 | > 1000 ug/L | | |
| | Al_{1113} | 396.152 | ug/L \| ug/L | 500-100 | > 5000 ug/L | 50 ug/L | 5.17 |
| | Ti_{1122} | 334.941 | ug/L \| ug/L | 200-100 | > 1000 ug/L | | |
| | B_{1105} | 249.773 | ug/L \| ug/L | 100-200-400 | 1000 ug/L | 50 ug/L | 7.40 |
| Pb in paint | Pb_{1682} | 220.353 | mg/L/%wt | 10-4-2 | 10 mg/L | .03 mg/L | |
| tclpplus | Cd_{1248} | 226.503 | mg/L \| mg/L | 5-2-1 | >5 mg/L | .1 mg/L | 5.12 |
| | Ba_{1256} | 230.427 | mg/L \| mg/L | 50-20-10 | > 50 mg/L | .1 mg/L | 4.56 |
| | Se_{1234} | 196.024 | mg/L \| mg/L | 5-2-1 | >5 mg/L | .3 mg/L | 5.69 |
| | Cr_{1224} | 267.708 | mg/L \| mg/L | 5-2-1 | >5 mg/L | .3 mg/L | 4.92 |
| | Ag_{1247} | 328.068 | mg/L \| mg/L | 5-2-1 | >5 mg/L | .1 mg/L | 5.07 |
| | As_{1233} | 193.697 | mg/L \| mg/L | 5-2-1 | >5 mg/L | .3 mg/L | 5.18 |
| | Pb_{1282} | 220.353 | mg/L \| mg/L | 50-20-10 | >50 mg/L | .5 mg/L | 4.90 |
| | | | | | | | |

Table 3. ICP Analyte Parameters

| Analyte | Analyte | Wavelength nm | Interferant | Estimated DL ug/L | DL | IDL |
|---|---|---|---|---|---|---|
| Al | Aluminum | 308.215 | V Mo Ce Mn Use 396.15 (Ca) | 45 | 50 | 8.2 |
| Sb | Antimony | 206.833 | Cr Mo Sn Ti Ce Fe | 32 | | |
| As | Arsenic | 193.759 | V Al Co Fe Ni | 53 | .04 | .04 |
| Ba | Barium | 493.409 | None | 2.3 | .02/.3 | .002/.1 |
| Be | Beryllium | 313.042 | V Ce | .27 | .2 | .1 |
| B | Boron | 249.678 | None (Fe) Use 208.893 | 5.7 | 50 | 16.2 |
| Cd | Cadmium | 226.502 | Ni Ti Fe Ce | 3.4 | .01 | .004 |
| Ca | Calcium | 315.887 | Co Mo Ce | 30 | .14 | .015 |
| Ce | Cerium | 413.765 | None | 48 | | |
| Cr | Chromium | 205.552 | Be Mo Ni | 6.1 | .01 | .01 |
| Co | Cobalt | 228.616 | Ti Ba Cd Ni Cr Mo Ce | 7.0 | | |
| Cu | Copper | 324.754 | Mo Ti | 5.4 | 2.2 | 2.9 |
| Fe | Iron | 259.940 | None | 6.2 | .01 | .007 |
| Pb | Lead | 220.353 | Co Al Ce Cu Ni Ti Fe | 42 | .07 | .09 |
| Li | Lithium | 670.784 | None | 3.7 | | |
| Mg | Magnesium | 279.079 | Ce | 30 | .08 | .047 |
| Mn | Manganese | 257.610 | Ce | 1.4 | .00 | .002 |
| Hg | Mercury | 194.227 | V Mo | 2.5 | | |

| Analyte | Analyte | Wavelength nm | Interferant | Estimated DL ug/L | DL | IDL |
|---|---|---|---|---|---|---|
| Mo | Molybdenum | 203.844 | Ce | 12 | | |
| Ni | Nickel | 231.604 | Co Tl | 15 | 8.9 | 12.4 |
| P | Phosphous | 214.914 | Cu Mo | 76 | | |
| K | Potassium | 766.491 | None | 700 | .05 | .031 |
| Se | Selenium | 196.090 | Fe | 75 | .06 | .06 |
| SiO2 | Silica | 251.611 | None | 26 | .22 | .3 |
| Ag | Silver | 328.068 | Ce Ti Mn | 7.0 | .006 | .006 |
| Na | Sodium | 588.995 | None | 29 | .2 | .051 |
| Sr | Strontium | 421.552 | None | .77 | | |
| Tl | Thallium | 190.864 | Ti Mo Co Ce Al V Mn | 40 | | |
| Sn | Tin | 189.980 | Mo Ti Fe Mn Si | 25 | | |
| Ti | Titanium | 334.941 | None | 3.8 | | |
| V | Vanadium | 292.402 | Mo Ti Cr Fe Ce | 7.5 | | |
| Zn | Zinc | 213.856 | Ni Cu Fe | 1.8 | | |

Table 4. Standard Preparation

| Method, std # | Stock Standard/Analyte | | Aliquot volume | Diluted to volume | Concentration |
|---|---|---|---|---|---|
| Cation-Sio2 **Std #1** | 1000 | Fe, Mn | 1.25 ml (625ul x2) | 500 ml | 2.5 mg/l |
| | 10000 | Si | 1.25 ml | 500 ml | 53.5 mg/l $SiO_2$ |
| | 10000 | K | 2.5 ml | 500 ml | 50 mg/l |
| | | Mg | 5 ml | 500 ml | 100 mg/l |
| | | Ca | 10 ml | 500 ml | 200 mg/l |
| | | Na | 25 ml | 500 ml | 500 mg/l |
| **Std #2** | 1000 | Fe, Mn | 500 ul | 500 ml | 1 mg/l |
| | 10000 | Si | 500 ul | 500 ml | 21.4 mg/l $SiO_2$ |
| | 10000 | K | l000 ul | 500 ml | 20 mg/l |
| | | Mg | 2 ml | 500 ml | 40 mg/l |
| | | Ca | 4 ml | 500 ml | 80 mg/l |
| | | Na | 10 ml | 500 ml | 200 mg/l |
| **Std #3** | #1 std | Fe,Mn Si | 50 ml and (add 125 ul Si) | 500 ml | .25/ 10.2 mg/l $SiO_2$ |
| Do 1:10 dilution of #1 | | K | | | 5 mg/l |
| std. | | Mg/Ca | | | 10/20 mg/l |
| | | Na | | | 50 mg/l |
| | | | | | |
| Cation-Sio2 **Std #5** | | Fe,Mn/Si | 500 ul | 100 ml | 5 mg/l /107.0 SiO2 |

| Method, std # | | Stock Standard/Analyte | Aliquot volume | Diluted to volume | Concentration |
|---|---|---|---|---|---|
| | | K | 1000 ul | 100 ml | 100 mg/l |
| | | Mg | 2000 ul | 100 ml | 200 mg/l |
| | | Ca | 4 ml | 100 ml | 400 mg/l |
| | | Na | 10 ml | 100 ml | 1000 mg |
| TCLP | **Std #1** | 1000 AsCdCrSeAg | 500 ul | 100 ml | 5 mg/l |
| | | 10000 BaPb | 500 ul | 100 ml | 50 mg/l |
| TCLP | **Std #2** | 1000 AsCdCrSeAg | 200 ul | 100 ml | 2 mg/l |
| | | 10000 BaPb | 200 ul | 100 ml | 20 mg/l |
| TCLP | **Std #3** | 1000 AsCdCrSeAg | 100 ul | 100 ml | 1 mg/l |
| | | 10000 BaPb | 100 ul | 100 ml | 10 mg/l |
| TCLP | **IPC** | Make same as #3 Std | | | |
| **Pb in Paint** | **Std #3** | 1000 Pb | 500 ul | 50 ml | 10 mg/l |
| | **Std #2** | | 200 ul | 50 ml | 4 mg/l |
| | **Std #1** | | 100 ul | 50 ml | 2 mg/l |
| | **IPC** | | 250 ul | 50 ml | 5 mg/l |
| | | | | | |
| | | | | | |
| | | | | | |
| | | | | | |
| **Alb** | **Std #1** | 1000 Al,B | 100 ul | 1000 ml | 100 ug/l |

| Method, std # | Stock Standard/Analyte | Aliquot volume | Diluted to volume | Concentration |
|---|---|---|---|---|
| **Std #2** | Al,B | 500 ul | 1000 ml | 500 ug/l |
| **Std #3** | Al | 500 ul | 500 ml | 1000 ug/l |
| | B | 100 ul | 500 ml | 200 ug/l |
| Alb **Std #4** | 1000 Al | 1250 ul | 250 ml | 5000 ug/l |
| **BCZsoils Std #1** | 1000 Ba, Cu, Zn, Al | 100 ul | 1000 ml | 100 ug/L |
| **Std #2** | Ba, Cu, Zn, Al | 500 ul | 1000 ml | 500 ug/L |
| **Std #3** | Ba, Cu, Zn, Al | 1000 ul 500 ul | 1000 ml 100 ml | 1000 ug/L 5000 ug/L |
| Any analyte | 1000 mg/L (ug/ml) | 50 ul | 1000 ml | 50 ug/L |
| | | 100 ul | 1000 ml | 100 ug/L |
| | | 200 ul | 1000 ml | 200 ug/L |
| | | 500 ul | 1000 ml | 500 ug/L |
| | | 1000 ul | 1000 ml | 1000 ug/L |
| | | 250 ul | 25 ml | 10,000 ug/L |
| | | | | |